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Industrial ceramic shaped body, process for producing it and its use

The invention relates to a fired, basic, refractory, industrial ceramic, elasticized shaped body based on at least one resistor component such as magnesia and doloma. In addition, the invention relates to a process for producing the shaped body and to its use.

Shaped bodies of the generic type are used as refractory lining, in particular in high-temperature processes involving attack by basic slag, e.g. in furnaces, tanks or vessels in the cement, lime, dolomite, magnesite, steel and nonferrous metals industries and also in the glass industry.

Although a shaped body composed of a resistor component (hereinafter also referred to simple as resistor) such as MgO or CaO/MgO (doloma) has a high fire resistance and good chemical resistance, it is generally brittle because it has a relatively high modulus of elasticity (E) and an unfavorable shear modulus (G). This has an adverse effect on, in particular, the dissipation of thermal stresses, the mechanical stressability and the thermal shock resistance (TSR). It is therefore desirable to set low elastic moduli because these are responsible for the thermomechanical durability.

To increase the elasticity or to reduce the elastic moduli, it is known that it is possible to add an elasticizer component (hereinafter also referred to simply as elasticizer) to a mix for producing a shaped body or to add raw materials which generate the elasticizer in the mix during ceramic firing.

For example, magnesia-chromite bricks or magnesia-spinel bricks which display usable shear moduli in the range from 8 to 12 GPa (gigapascal) are produced using chromium ores or synthetic spinel.

Refractory bricks containing molten hercynite or molten zirconium oxide as elasticizer have a low elasticity but are ductile. The shear moduli are from about 15 to 20 GPa and therefore relatively high.

These known elasticized, basic, refractory shaped bodies are evaluated, in particular, in respect of elasticity, desired deposit formation in a rotary tube furnace, redox resistance, alkali resistance, hydration resistance and disposability, with each of these known shaped bodies having, in terms of these properties, advantages and disadvantages, which can be seen from the following table:

Table 1: *Qualitative properties of known shaped bodies*

	Magnesia-spinel brick	**Magnesia-hercynite brick**	**Magnesia-chromite brick**	**Magnesia-zirconia brick**	**Dolomite brick**
Elasticity	good	poor	good	good	poor
Deposit formation	poor	good	good	poor	good
Redox resistance	good	poor	poor	good	good
Alkali resistance	good	poor	poor	good	poor
Hydration resistance	good	good	good	good	poor
Disposability	good	good	poor	good	good

Magnesia-spinel bricks and magnesia-zirconia bricks form a stable deposit in a rotary tube furnace only with difficulty; they consequently have only limited usability in, for example, the sintering zone of a rotary tube furnace for cement. Although magnesia-hercynite bricks display good deposit formation (cf. Variation of Physical and Chemical Parameters as a Tool for the Development of Basic Refractory Bricks; Klischat, Hans-Jürgen, Dr.; Weibel, Guido - REFRATECHNIK GmbH, Germany in Unified International

Technical Conference on Refractories, PROCEEDINGS, 6th Biennial Worldwide Congress in conjunction with the 42nd International Colloquium on Refractories, Refractories 2000, BERLIN - Germany 6-9 September 1999, 50 Years German Refractory Association; pages 204-207), they have a poor redox resistance and alkali resistance. The same applies to magnesia-chromite bricks which are additionally known to create disposal problems. Dolomite bricks containing no elasticizer do ensure very good deposit formation but are neither sufficiently alkali resistant nor sufficiently hydration resistant.

It is an object of the invention to provide a basic, elasticized, refractory shaped body which combines high fire resistance and good chemical resistance with, in particular, good elasticity and good deposit formation capability, and good redox, alkali and hydration resistance and can be disposed of without problems.

This object is achieved by the features of claim 1. Advantageous embodiments of the invention are defined in the subordinate claims and the other claims.

According to the invention, sintered magnesia and/or fused magnesia or sintered doloma and/or fused doloma, selected from among the numerous known resistors, is/are used as basic resistor. Calcium aluminate having a CaO/Al_2O_3 ratio of from 0.14 to 0.2, in particular of the chemical composition $CaAl_{12}O_{19}$ having the oxide formula $CaO \cdot 6Al_2O_3$ or the abbreviated formula CA_6, has been found as elasticizer.

Calcium hexaaluminate has the chemical formula $CaAl_{12}O_{19}$ or the mineral name "hibonite" and the oxide formula $CaO \cdot 6Al_2O_3$ or the abbreviated formula CA_6.

The Al_2O_3 of the CA_6 obviously does not react with the alkali metal and calcium compounds, e.g. in the rotary

tube furnace for cement, because it is already saturated with CaO. This results in a very good corrosion resistance. The CaO in the CA_6, which is also the main constituent of the cement clinker material, probably ensures very effective deposit formation in the rotary tube furnace, which cannot be achieved even with the deposit-forming, known, elasticized, refractory shaped bodies such as magnesia-hercynite bricks or magnesia-chromite bricks.

CA_6 is not an unknown in refractory materials. A refractory shaped body whose mineral oxidic component is formed by a mineral phase mixture of α-Al_2O_3, β-Al_2O_3, CA_6 and CA_2 is known from DE 199 36 292 C2. The mineral phase mixture is said to increase the corrosion resistance of the shaped bodies. CA_6 does not play an elasticizing role here.

The invention is illustrated below with the aid of an example:

Magnesia having a maximum particle size of 4 mm and a particle size distribution corresponding to a typical Fuller curve and the mineral calcium hexaaluminate having a particle size range from 0.5 to 4 mm were mixed, admixed with a required amount of lignin sulfonate as binder, shaped to form bricks and pressed at a specific pressing pressure of 130 MPa. After drying at 110°C, the bricks were fired at a sintering temperature of 1600°C in a tunnel kiln.

The achieved properties of the fired bricks as a function of the amount of calcium hexaaluminate added are shown in table 2 below. A magnesia brick fired in the same way was employed as comparison.

Table 2: *Properties of shaped bodies according to the invention compared to properties of a magnesia brick*

Magnesia	**% by mass**	100	92	84	76
CA_6	**% by mass**	-	8	16	24
Overall density	**g/cm^3**	2.99	2.99	2.98	2.97
Porosity	**%**	16.12	16.26	16.42	16.41
CCF	**MPa**	75.30	72.20	71.10	71.40
CFS	**MPa**	12.10	6.10	5.80	5.50
Modulus of elasticity	**GPa**	91.90	31.20	27.10	22.80
Shear modulus	**GPa**	41.50	12.80	11.40	10.60
TSR		15	>100	>100	>100

It can be seen from table 2 that the bricks according to the invention are sufficiently elasticized for use in a rotary tube furnace for cement with its temperature-dynamic conditions. The elastic moduli are within a very good range. The thermal shock resistance (TSR) is excellent.

The mechanism which leads to the very good elasticization of the bricks has hitherto not been able to be determined unambiguously. There is presumably microcrack formation between the magnesia matrix and the calcium hexaaluminate during firing of the bricks, caused by the difference in the thermal expansion of these two materials.

Table 3 below shows the individual relevant properties of the known shaped bodies of table 1 and those of the shaped bodies according to the invention.

Table 3: *Qualitative properties of known shaped bodies compared to a shaped body according to the invention*

	Magnesia-spinel brick	**Magnesia-hercynite brick**	**Magnesia-chromite brick**	**Magnesia-zirconia brick**	**Dolomite brick**	**Magnesia-CA_6 brick**
Elasticity	good	poor	good	good	poor	good
Deposit formation	poor	good	good	poor	good	good
Redox resistance	good	poor	poor	good	good	good
Alkali resistance	good	poor	poor	good	poor	good
Hydration resistance	good	good	good	good	poor	good
Dispos-ability	good	good	poor	good	good	good

Table 3 shows that all the types of brick known hitherto have significant disadvantages in terms of the application-relevant properties. In contrast, the magnesia-CA_6 bricks of the invention have exclusively good properties, as have hitherto not been known in their use-relevant combination.

Shaped bodies according to the invention can be used advantageously wherever severe temperature changes occur and wherever mechanical and thermomechanical stresses occur. These are, for example, sintering and transition zones of rotary tube furnaces in the brick and earth industry, in particular the cement, lime, dolomite and magnesite industries, ferrous and non-ferrous metals industry and also melting and handling vessels in the iron or steel industry and the non-ferrous metals industry. A shaped body according to the invention displays excellent use performance in respect of hydration, alkali, redox and corrosion resistance combined with good deposit formation tendency. It is thus also superior to the known products after use

because of unproblematical disposal possibilities.

The elasticization of the basic shaped bodies according to the invention can be achieved using not only pure calcium hexaaluminate, but it is also possible for secondary phases, e.g. SiO_2 and/or TiO_2 and/or Fe_2O_3 and/or MgO, to be present in amounts of up to 10% by mass in the calcium hexaaluminate. Furthermore, the calcium hexaaluminate also has the action described when up to 58% by mass of the Al_2O_3 has been replaced by Fe_2O_3 or when Ca^{2+} has been partly replaced by Ba^{2+} or Sr^{2+}, as indicated in "Trojer, F.: Die oxydischen Kristallphasen der anorganischen Industrieprodukte", E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart 1963, page 272.